

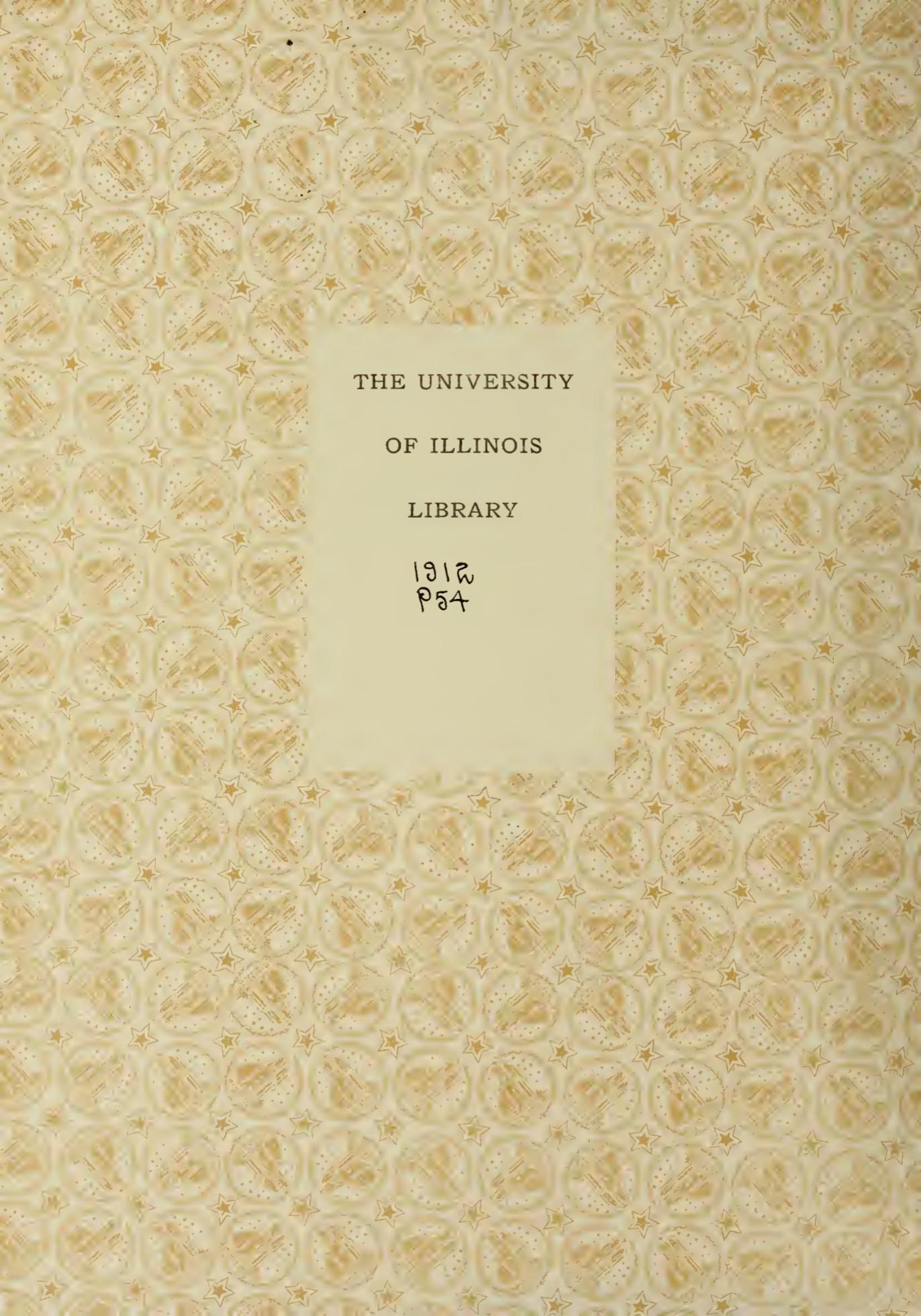
PHILLEO

The Properties of
Superheated Ammonia Vapor

Mechanical Engineering

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THE PROPERTIES OF SUPERHEATED AMMONIA VAPOR

BY

GEORGE WEST PHILLEO

T H E S I S

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

MECHANICAL ENGINEERING

COLLEGE OF ENGINEERING

UNIVERSITY OF ILLINOIS

1912

1912
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June 1st, 1912.

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

George West Philleo

ENTITLED --

The Properties of Superheated Ammonia Vapor

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

Bachelor of Science in

Mechanical Engineering.

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THE PROPERTIES OF SUPERHEATED AMMONIA VAPOR.

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THE PROPERTIES OF SUPERHEATED AMMONIA VAPOR.

I.

PURPOSE OF INVESTIGATION

The use of ammonia in refrigeration was introduced in 1850 and has been almost exclusive since 1880, yet the properties of this vapor are not well determined today even in the saturated region, while almost nothing has been done heretofore toward the investigation of the superheated vapor. In the ammonia compression type of refrigerating machine, unless special means is taken to prevent, the medium is compressed to a point well within the superheated region. In order, therefore, to properly design and operate such a machine it is necessary that the properties of the superheated as well as the saturated vapor be known.

In this investigation it is proposed to show that the equations representing the properties of ammonia vapor are in every way analogous to those derived for steam. The equations which have been used are those determined by Professor Goodenough for the volume, specific heat at constant pressure, the heat content and the Joule-Thomson coefficient $\frac{\Delta T}{\Delta P}$, and the object of the investigation has been the determination of the constants which will make those equations represent the values of the same properties for ammonia.

It is evident that if the functions $V = f(p, t)$ and $C_p = \Phi(p, t)$ are known, then the expressions for heat content and $\frac{\Delta T}{\Delta P}$ can be derived directly by mathematical methods. Yet it is not true that every equation which will give accurate values of volumes and specific heats will be the expression from which to derive the remaining equations. It is necessary, therefore, that the values

obtained from the equations for volume, specific heat and heat content be carefully compared with all the available experimental values before final selection of the constants is made. When a selection has been made which accurately represents these three properties, it is safe to assume that the same constants may be used in the expression for $\frac{\Delta T}{\Delta P}$, and any data corroborating this property will strengthen the entire structure of our theory.

This work has been done in connection with the more extended work of Professor Goodenough and Mr. Mosher embracing the properties of liquid, saturated, and superheated ammonia; and this thesis must be considered rather as a preliminary report on one branch of the subject than as a finished work.

II.

AVAILABLE DATA.

The experimental data from which it was necessary to determine the constants for the various equations are very meagre in the superheated region. Four volumes at atmospheric pressure and at the temperatures of -4° , 32° , 120° , and 212° F. and one volume at one half atmospheric pressure and at 32° F. have been observed by Perman.¹ Le Duc² and Guye have each determined the volume at atmospheric pressure and 32° F., their observations agreeing with that of Perman at that point. No other absolute volume of the superheated vapor have been observed, but the experiments of Regnault³ furnish

1. Proc. Royal Soc. Vol. 78A, p. 28, 1906.

2. Comptes Rendus, Vol. 125, p. 571, 1897, and Vol. 141, p. 51, 1905.

3. Mem. de l'Inst. de France, Vol. 26, p. 252, 1862.

data on the relative change in volume at 46.58° F. for thirteen different pressures. Regnault measured the volumes at these different pressures, but did not record the weight of the vapor used, so that the actual specific volume cannot be known from his work. His results ^{furnish} important corroborative evidence, however, which will be shown in the discussion of the results of the volume investigation. The values of volume along the saturation curve were obtained from the equation of Professor Goodenough and Mr. Mosher which will soon be published in a bulletin of the University of Illinois Experiment Station. This equation is a mere smoothing up of the volume determinations of Dieterici¹; and expresses them with great accuracy. The saturation curve is, of course, the locus of the points of zero superheat and may thus be used as the terminus of all isothermals on the p - v plane.

The values of specific heat are those given by Nernst², and include not only his own determinations at high temperatures, but also those of Keutel, Voller, and Wiedeman at lower temperatures, and they comprise practically all that has been done along this line. From Van Strombeck³, A. J. Wood⁴, and Elleau and Ennis⁵, however, several points have been determined on the specific heat of the liquid ammonia, and have been used to advantage in checking results.

The only available data on the heat content are those of

-
1. Zeitschrift für die Gesamte Kalte - Industrie, 1907, p. 61 and personal letter.
 2. Zeitschrift für Elektrochemie. Vol. 16, p. 96, 1910.
 3. Jour. Frank. Inst. Jan. 1891, and Dec. 1890.
 4. Ice and Refrigeration, April, 1912.
 5. Jour. Frank. Inst. April, 1898.

Dieterici and Drewes. Their determinations form the basis of our investigation of this property, yet, as will be shown later, they were in reality data on the change in intrinsic energy of the liquid rather than on total heat.

A discussion of the Joule-Thomson coefficient $\frac{\Delta T}{\Delta P}$, more generally known as μ , is given by Davis¹ in a paper on the law of corresponding states. In this paper he shows that the law holds for steam and carbon dioxide, and draws the conclusion that all vapors must obey that law. The only direct determinations of the coefficient for ammonia were made by Wobsa, some discussion of which will be given later.

The insufficiency of the data as a basis for an independent investigation is at once apparent. At the same time, they are so well distributed over the various properties under discussion that, when equations representing so well the properties of steam are used, and constants are found which make them agree with the known data, there should be little question but that these equations will be reliable for interpolation, if not for extrapolation.

III.

DERIVATION OF PRINCIPLE EQUATIONS AND CONSTANTS.

I.

Characteristic Equation.

The characteristic equation of Linde for superheated steam

$$pv = BT - p(1 + ap) \left[C \left(\frac{373}{T} \right)^n - D \right]$$

has been modified by Professor Goodenough to take the form

$$v + c = \frac{B T}{p} - (1 + ap) \frac{m}{T^n}$$

The most convenient coordinates in which to show the pressure-vol-

¹. Proc. Amer. Acad. Arts and Science, Vol. 45, p. 243. 1909.

ume-temperature relation are $p v$ and p . For plotting in these coordinates the equation takes the more convenient form

$$p v + p C = B T - p(1 + a p) \frac{m}{T^n}$$

Since determinations of volume had been made for but four different temperatures of superheat, and since in but one case - namely 32°F - had two points been determined on the isothermal, there were in each case, save one, but two points known for each isothermal - the point on the saturation curve and the one in the superheated region. It was at first thought that these isothermals might be straight lines, so a rational method of determining the constants was employed. In order that these lines be straight the constant a must become zero. The first derivative of the function with T held constant then be-

$$\text{comes } \left[\frac{\partial p v}{\partial p} \right]_T = - \frac{m}{T^n} - c$$

and this derivative must represent the slope of any isothermal.

Since the four isothermals were determined by the location of two points on each line, the value of the derivative was known for each of the four temperatures, and the constants were readily determined. From general considerations, the value of n was taken as 5, so that it was possible to solve for the values of m and c by the solution of all the combinations of two of the four equations of the isothermals. The mean values of the two constants were then chosen as those which would best determine the volume relations. The equation thus derived was found to express quite accurately the experimental determinations both in the superheated region and along the saturation curve, but when

the same constants were substituted in the expression for heat content it became evident that the constant a must not be made equal to zero. On further consideration, too, it seemed wise for theoretical reasons not to make the isothermal a straight line, since, in the case of steam, these lines are quite noticeably parabolic, and it appears desirable to maintain the analogy. It was found, moreover, that the volumes could be determined with almost equal accuracy for a considerable range of values of a and the corresponding values of m and c, so the final selection of these constants was left to be determined in connection with the investigation of the other properties. It is, of course, evident, that the various properties are so interconnected that the determination of any of the constants cannot be final until an agreement has been reached throughout the entire discussion. The volume determinations were used as a basis, however, and they placed the limits within which the constants might be varied in the further investigation.

2.

Equation for Specific Heat.

From the characteristic equation and general thermodynamic relations an expression for the specific heat at constant pressure was derived. Thus

$$dq = C_p dT - AT \left(\frac{\partial v}{\partial T} \right)_p dP$$

and $di = dq + AvdP$

hence $di = C_p dT - A \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dP$

Since di is an exact differential, not dependent on the path but

dependent on the state only,

7

$$\left(\frac{\partial C_p}{\partial p}\right)_T = - AT\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

From the characteristic equation

$$v + c = \frac{BT}{p} - (1 + ap) \frac{m}{T^n}$$

$$\frac{\partial v}{\partial T} = \frac{B}{p} + n(1 + ap) \frac{m}{T^{(n+1)}}$$

and
$$\frac{\partial^2 v}{\partial T^2} = - n(n+1)(1+ap) \frac{m}{T^{(n+2)}}$$

From which
$$\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{An(N+1)(1+ap)m}{T^{(n+1)}}$$

Integrating, the value of C_p is found to be

$$C_p = \frac{An(n+1)m}{T^{(n+1)}} p\left(1 + \frac{a}{2}p\right) + C$$

where C is a constant of the integration. Since T was held constant in the integration, this term C may be a function of T.

It is evident that as T becomes great the term involving T becomes small, so that for very high temperatures the value of C_p becomes equal to the function of T, which entered as the integration constant. From Nernst we have the equation for molecular specific heat

$$C_p = 8.62 + 0.002t + 7.2 \frac{t^3}{109}$$
 where t is in degrees centigrade. Changing to Fahrenheit degrees, we have

$$C_p = 8.62 + 0.002 \times \frac{5}{9}(t - 32) + 7.2 \left(\frac{5}{9} \frac{t-32}{109}\right)^3$$

reducing this term and dividing by 17.064, the molecular weight of ammonia, we have
$$C_p = 0.50307 + 0.00006533t - 0.06944 \frac{t^2}{10^7} + 0.07235 \frac{t^3}{10^9}$$
 in B.T.U.s per degree F.

The accompanying table gives the experimental and calculated values of specific heat given by Nernst and shows the accuracy of the equation just given.

<u>Observer.</u>	<u>Temp. C.</u>	<u>Observed.</u>	<u>Computed.</u>	<u>Diff.</u>
Keutel	20	8.64	8.66	+ 0.02
Voller	20	8.62	8.66	+ 0.04
Wiedemann	25 - 100	8.84	8.74	-0.10
"	25 - 200	9.11	8.86	-0.25
Regnault	24 - 216	9.71	8.88	+ 0.17
Nernst	365 - 567	10.4	10.3	-0.10
"	480 - 680	11.2	11.2	0.0

It will be noticed that there is no pressure term in the Nernst equation, although it is known that with steam the specific heat varies with the pressure. Further examination of Nernst's data disclosed the fact that all the experiments were carried on at or near atmospheric pressure. The equation would then simply carry the pressure term in with the constants. It is also known that the specific heat curve of steam is not nearly straight at low temperature, as would be the case with the Nernst equation. The equation may be used, however, as a means of determining the function of T which entered from the integration. Inspection will make evident the fact that up to temperatures of 700° or 800° the second and third degree terms in t may be entirely neglected without sensibly affecting the accuracy of the expression. The function of T then takes the form $\alpha + \beta T$, where α and β are constants to be determined, and the expression for specific heat becomes

$$C_p = \alpha + \beta T + \frac{An(n+1)m}{T(n+1)} p \left(1 + \frac{a}{2} p\right)$$

The constants α and β are readily determined when the constants of the characteristic equation are known, but it was found that

small changes in the latter equation had little effect in the specific heat determination, so the final selection of the constants was left for the investigation of the heat content.

3.

Equation for Heat Content.

From the relation $dq = C_p dT - AT \left(\frac{\partial v}{\partial T} \right) dp$ and the definition $i = A(u + pv)$

we have $di = dq + Avdp$

and $di = C_p dT - A \left(T \frac{\partial v}{\partial T} - v \right) dp$

From the characteristic equation we have

$$\frac{v}{T} = \frac{B}{p} + n(1 + ap) \frac{m}{T(n+1)}$$

$$\begin{aligned} \text{and} \quad di &= \alpha + \beta T + Amn(n+1)p \left(1 + \frac{a}{2} p \right) \frac{dT}{T(n+1)} \\ &\quad - \frac{Am(n+1)}{T^n} (1 + ap) dp - Acdp. \end{aligned}$$

The differential is exact, so that, integrating,

$$i = \alpha T + \frac{\beta}{2} T^2 - A(n+1)p \left(1 + \frac{a}{2} p \right) \frac{M}{T^n} - ACp + i_0,$$

i_0 being a constant of integration.

This equation having been deduced, it became necessary to select definitely the constant involved. Before this step is taken up, however, some slight explanation of the experiments on the determination of heat content is necessary. As before mentioned, these experiments were made by Dieterici and Drewes, those of Drewes having been made under the supervision of Dieterici. Some criticism has been aroused by the fact that only five grams of ammonia were used in these measurements, the customary amount in

such work usually being about fifty grams. Nevertheless, the work seems to have been done with a great deal of care and the results seem quite consistent, so that no hesitation was felt in using them. A known quantity of ammonia liquor and vapor was sealed in a strong glass tube graduated so that the volume of the liquor could be measured. The tube and contents were heated to a given temperature, the volume reading taken, and the tube then plunged into a Bunsen ice calorimeter where its temperature was reduced to zero degrees Centigrade. A blank test was run at the same time on a similar empty glass tube to determine the specific heat of the glass. The heat given up by the ammonia could thus be measured with great accuracy. Since the ammonia was in a sealed tube, no work was done on it or by it, and the equation $dq = du + dw$ becomes $dq = du$. The heat measured was, therefore, the change in intrinsic energy in the liquid and vapor. From thermodynamic considerations it can be shown that this heat is

$$Q_{12} = (m \rho)_0^t + MC_{pm} t$$

where C_{pm} is the mean specific heat of the liquid and ρ is the latent heat of the vapor. The value of ρ was known from previous experiments so that the value of the expression $C_{pm} t$ could readily be determined. This term, then, is the intrinsic energy, u , given up by the liquid. Now the heat content

$$i = u + Apv$$

so, in order to determine the values of heat content of the liquid it was necessary to add the term Apv to the value of energy found from the experiment. The zero of energy was arbitrarily chosen at 32° F so that the heat content at 32° F . is always equal to the value of Apv . at this point.

Having thus established bases on which to found the equation the method of determining the constants will now be taken up. Different values of a from 0 to 0.0006 were chosen, and the values of B , m , and C which would maintain the accuracy of the volume equation were found by the method of "cut and try". In determining α and β a more rational method was used. The equation of Nernst is represented by what is practically a straight line up to a temperature of about 700 degrees. The equation deduced in this investigation is represented by a practically straight line from 200 degrees upward. It was not considered necessary that the expression should be accurate for higher temperatures than 700 degrees, so from the values of the Nernst equation at 200 and at 700 degrees were subtracted the values of the term $(1 + \frac{a}{2}p) \frac{Amn(n+1)}{T(n+1)}$ for atmospheric pressure and the same temperatures, and the remainders were two points on the straight line $\alpha + \beta T$. These two constants could then be readily determined. The values of the expression for heat content

$\alpha T + \frac{\beta}{2} T^2 - A(n+1)p(1 + \frac{a}{2}p)\frac{m}{Tn} - Acp$ were then calculated. This expression, which is, of course, equal to $i - i_0$ can be determined from the observed values of the heat of the liquid. Thus

$$i = i' + i'' + r$$

where i is the total heat content, i' is the heat of the liquid, i'' the heat content of superheating, and r is the heat of vaporization. The value of r at saturation was known from the equation of Professor Goodenough and Mr. Mosher, the term i'' is, of course, zero at saturation, so that, subtracting, from the sum $r + Apv$ for 32° the value of the above expression for $i - i_0$ at

the same temperature, the result is the constant of integration, i_0 . Using this constant as determined with the various sets of constants the values of that group were chosen which gave results comparing most favorably with the data for the temperature range which it was desired to cover; namely, from -4° to 200°F . The final selections were as follows:

$$C = 0.075$$

$$m = 8.897 \times 10^{12} \qquad \log. m = 12.949244$$

$$B = 0.6321 \qquad \log. B = .800786$$

$$i_0 = 345.0$$

$$\beta = 0.000125$$

$$\alpha = 0.425$$

$$A = 0.0003$$

4.

The Joule-Thomson Coefficient.

Coming now to the Joule - Thomson coefficient μ , it will be necessary to define its meaning and to discuss the method of its determination. If a gas at a given pressure and temperature is forced through a porous plug into a region of lower pressure, there will be a change in temperature. The changes taking place in this process, usually known as throttling, are shown thus. The vapor in its original state has an energy u ,; in passing through the plug it does a frictional work Z and in moving through a displacement v , with pressure p . there is work done on the gas or vapor $p.v$. The work Z is turned into heat and given back to the vapor; in passing through a displacement v_2 at pressure p_2 the gas does

work $p_2 v_2$; and in its second state it has an intrinsic energy u_2 .

There was no heat added or taken away in the process, so that the energy before passing through the plug equals that in the second state and

$$u_1 + p_1 v_1 = u_2 + p_2 v_2 \quad \text{or } i_1 = i_2$$

The Joule - Thompson coefficient is the rate of change of temperature with the pressure and is, therefore,

$$\mu = \left(\frac{\partial T}{\partial p} \right)_i = - \frac{\frac{\partial i}{\partial p}}{\frac{\partial i}{\partial T}}$$

The derivative $\frac{\partial i}{\partial T}$ is evidently the specific heat at constant pressure C_p . and therefore

$$\mu = - \frac{1}{C_p} \frac{\partial i}{\partial p} = \frac{A}{C_p} \left[- \frac{m(n+1)}{T^n} (1 + ap) \right] + C$$

The form of this equation might, at first glance, seem to indicate values of μ increasing with the pressure. Such, however is not the case, as the specific heat, increasing with the pressure decreases the value of μ , more than offsetting the effect of the pressure term. The experimental determination of this coefficient is made by measuring the slope of the pressure temperature curve found from throttling experiments. Now the law of corresponding states says that, if these values of μ are "reduced" by multiplying by the ratio of the critical pressure of the vapor to its critical temperature, and are plotted against the corresponding "reduced" temperature, which are the ratios of the actual absolute temperature to the critical temperature, then the resulting curve will be the same for all vapors. The results of following this method in the present investigation will be discussed in the comparison of data and equations.

IV.

COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS.

The accuracy of the expressions which have now been derived will be evidenced by comparison with the experimental determinations. All known data have been used in this investigation, and comparisons will be shown as fully as possible, for, though it must be expected that with observations gathered from so many sources, some will be inaccurate, nevertheless it is desirable that every opportunity be taken for corroborating or confuting the equations before they are accepted as final. Inaccurate data are not infrequently not consistent in their general trend with accurate data, thus making evident the fact that they are not to be relied upon. Where such inconsistencies occur the evidence of the majority must be accepted unless errors of method can be shown.

1.

Volumes.

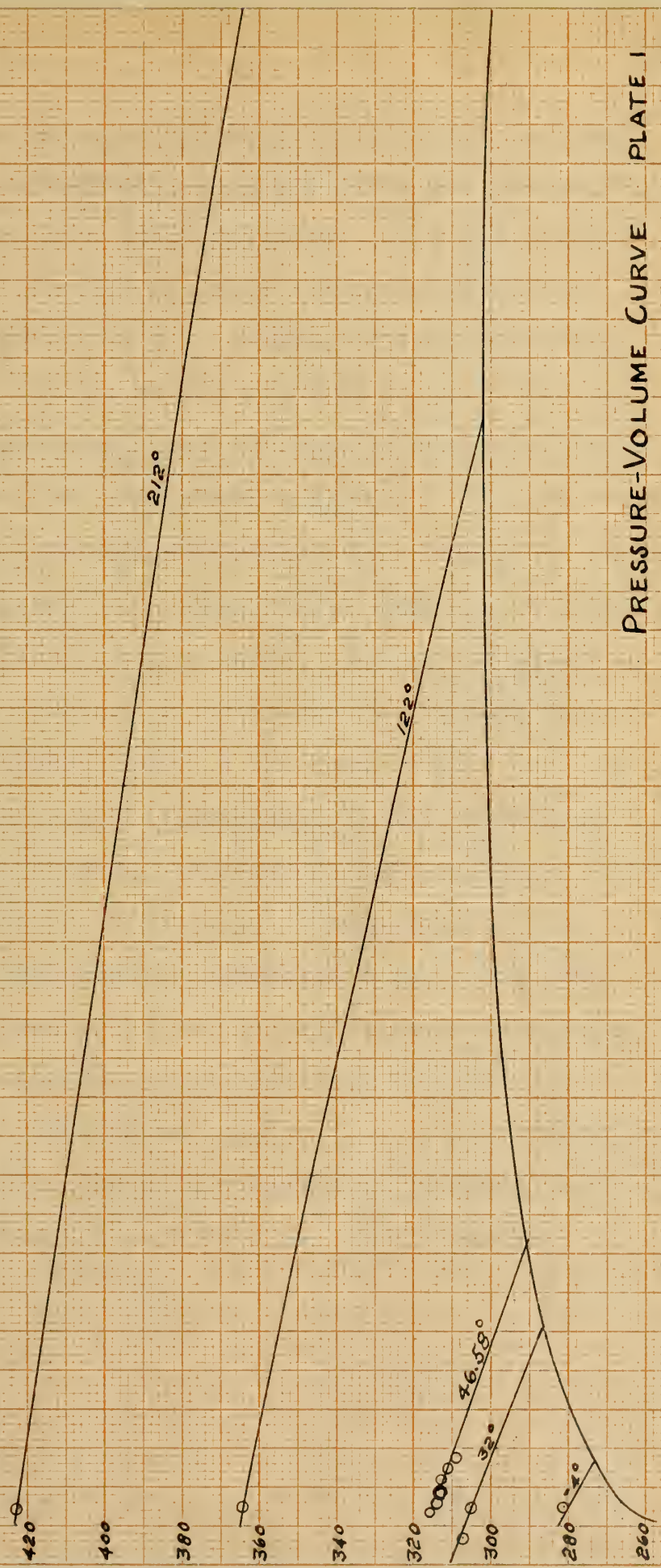
The saturation curve on the p - p_v plane, Plate I, was plotted from the equation for saturated vapor, though it might equally well have been plotted from the characteristic equation for the superheated vapor, as the agreement is so close as to render differences invisible on the scale of this chart. The isothermals, however, were plotted from the latter equation. The points shown on these curves are all Perman's except those on the 46.58° isothermal which are Regnault's. In order to use the Regnault points a reducing factor was found by which they

PRESSURE-VOLUME CURVE

PLATE I

P

pv



might be changed to the units of the scale here used. In doing this the middle point on Regnaults original curve was chosen, and the pressure transferred into ordinary units. From the present equation the volume and product $p v$ were determined for this pressure. Dividing this by the $p v$ corresponding to the point chosen on the Regnault chart gave the required factor. The result is to make the isothermal pass through the middle of the Regnault points, so that the only check afforded is that of slope. Such evidence is helpful though not conclusive. The close agreement of the volume equation with experimental data can be shown more precisely by the accompanying table. The errors within the range which it is necessary to cover are well within the range of experimental error except in the case of the -4° isothermal. There is considerable discrepancy in this case, yet not more than is often found in the work of the best experimenters, and further data on this point would be of much value. The isothermals although retaining the parabolic form, due to the term $(1 + a p)$ are, nevertheless, so nearly straight that this term might have been omitted without affecting the result to an appreciable extent. The volume equation, as it now stands seems to be as accurate as the data on which it is based, so that, until more experimental work is done, no changes are necessary.

Deg. F.	Press.	Observed Volume.	Computed Volume.	Error.
Saturated.				
-40	10.12	25.4520	25.450	-0.0020
-20	17.91	14.8945	14.8960	0.0015
0	29.95	9.1874	9.1924	0.005
20	47.75	5.9201	5.9347	0.0146
40	73.03	3.9595	3.9581	-0.0014
60	107.7	2.7344	2.7324	-0.0020
80	153.9	1.9400	1.9394	-0.0006
100	213.8	1.4087	1.4071	-0.0016
120	289.8	1.0427	1.0416	-0.0011
140	384.4	0.78395	0.7830	-0.00095
160	500.1	0.59656	0.59619	-0.00037
180	639.5	0.45771	0.45814	0.00043
200	805.6	0.35250	0.35417	0.00167
Super Heated				
-4	14.696	19.154	19.0680	-0.086
32	"	20.780	20.760	-0.020
122	"	24.784	24.808	0.024
212	"	28.774	28.749	-0.025
32	7.348	41.810	41.907	.097

SPECIFIC HEAT CURVE

PLATE II

7

1000

900

800

700

600

500

400

300

200

100

50

Cp

.66

.62

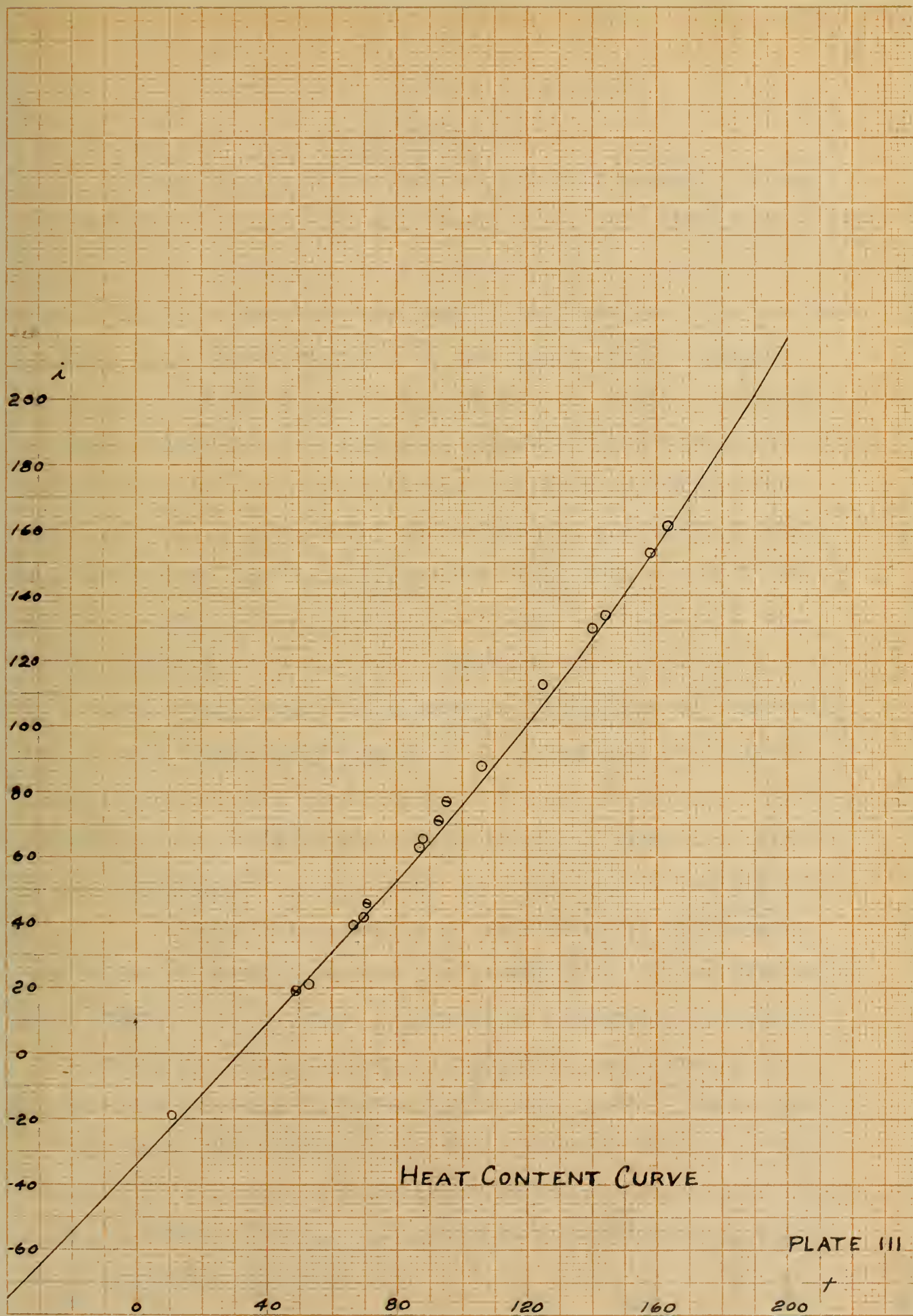
.58

.54

.52

Specific Heats.

The success with the equation for specific heat was not so marked, the error which exists there coming from the assumption that the equation of Nernst was correct for the middle and upper ranges of temperature. It is true that his expression does represent quite well the data shown, but an inspection of the curve of specific heat, Plate II, will show that the data were grouped at the ends of the range. There is no reason to suppose that the curve should run straight from the lower range along an asymptote much lower than the points at the upper range and then suddenly rise so as to agree with those points, as is the case with Nernst's equation. From the analogy with steam it is much more reasonable to suppose that the curve has a steeper asymptote, thus representing the values at the upper range without using the higher degree terms in the equation. Still, it was not considered necessary, as before stated, to find an equation of extreme accuracy at the upper range of temperatures, and, imperfect as the present expression is, it is a step in the direction of a reliable equation. Nor can this expression be counted extremely bad, for the errors are much exaggerated by the largeness of the scale used, and are, in reality, not such as to cause errors of consequence in engineering calculations. More work is being done in this part of the investigations, so that, even now, better results have been obtained, and it is expected that the bulletin which is soon to be published will contain expressions fully as accurate as the known data makes possible.



Heat Contents.

The results of the work on the heat content, though not perfect, are much more encouraging than with the specific heat. Reference to the curve of heat content plotted against temperature Plate III, will show the agreement of the equation with the data at hand. The points marked with the circle with a diagonal cross bar are those determined by Dieterici, while those with the open circle are the result of Drewes's work, much of it under the supervision of Dieterici. It will be noticed that the curve lies almost wholly on one side of the band of points. The explanation for this discrepancy comes from the fact, which developed late in the investigation, that the heat unit used by these two investigators differed from the now accepted unit by a small though appreciable amount. The points as originally transferred from calories to B. T. U. s lay well distributed along the curve, but the mistake, which was discovered from a personal letter from Professor Dieterici was known too late to permit changing the constants of the equations in the discussion.

Further corroboration of this equation is given by the values of specific heat of the liquid given by Van Strombeck, Wood and Elleau and Ennis. In order to compare the equation with these data the graphical tangents to the curve at the temperature for which data was known were found. These tangents, since they represent the first derivatives of the equations, give the values of the specific heat at the points where they are taken. The results are given in the following table which shows the agreement.

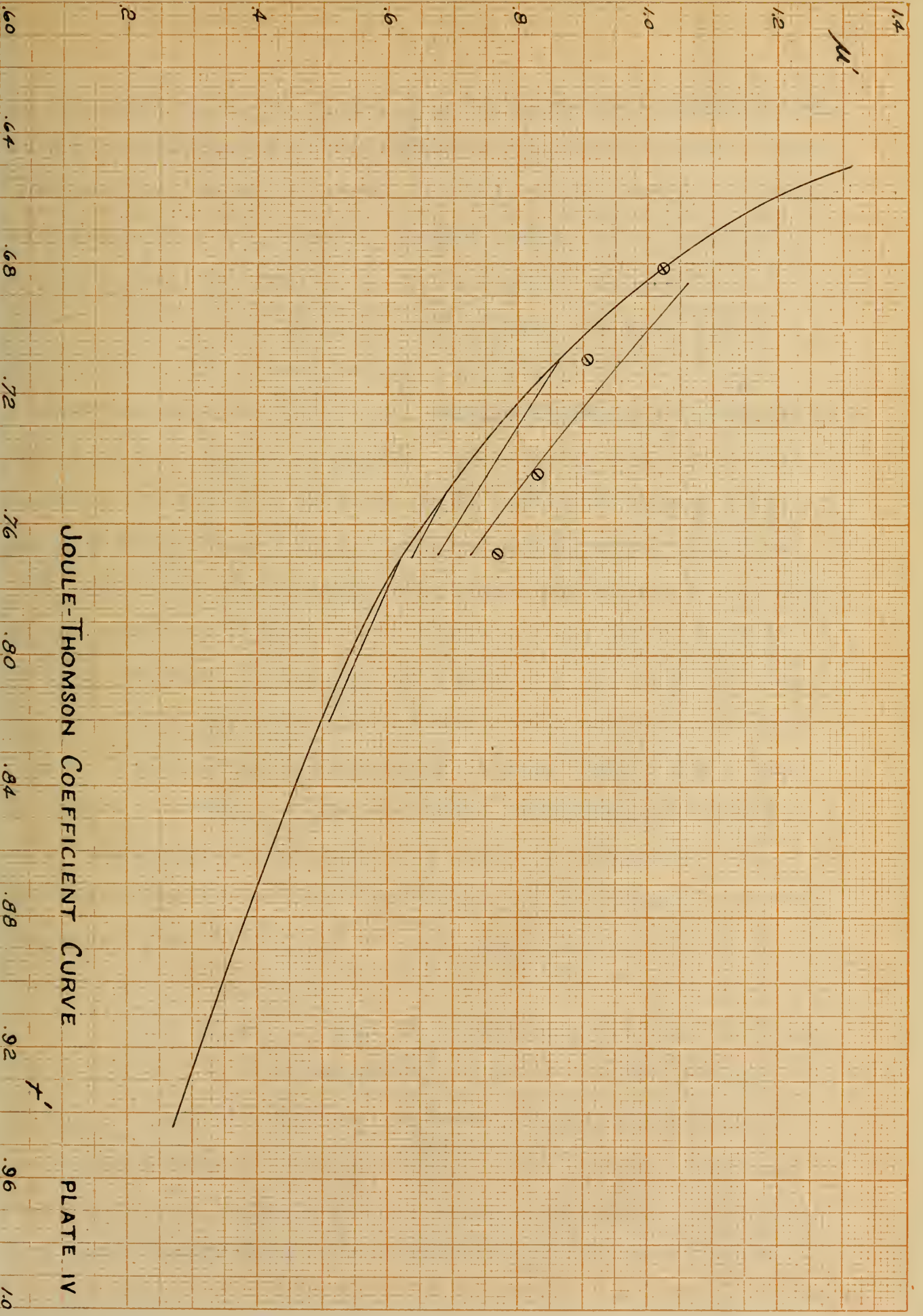
Authority	Temperature in Degrees F.	c Observed	c from curve.
Van Strombeck	112	1.22876	1.23
Wood	60 - 70	1.094	1.10
Elleau & Ennis	50	1.02	1.08

Now, since the curve must pass through zero plus Ap_v at 32°F . and since the slopes are so accurately determined, there can be little question as to its practical correctness. It must be remembered that the results here shown are the heat contents of liquid, found by subtracting the heat of vaporization from the heat at saturation, the latter being the result of the solution of the equation for superheated vapor. The heat of vaporization is known to be substantially correct, but there is no confirmation of the equation from the superheat side. The analogy with steam must again be called upon to aid us in upholding the validity of the theory.

4

The Joule - Thomson Coefficient.

When the experimental determinations by Wobsa of the Joule - Thomson coefficient were found, it was hoped that they would materially strengthen the theory of this work. Such, however, was found not to be the case, in fact, the disagreement was quite decided. As this was the only data on this coefficient for ammonia, it was necessary to go to the law of corresponding states, not only for confirmation of the equation, but, if possible for refutation of Wobsa's data. The general curve, Plate IV, is that found by Davis to represent



JOULE-THOMSON COEFFICIENT CURVE

PLATE IV

in "reduced" units the values of μ for steam and carbon dioxide. It was derived from extensive data on steam and from the Joule - Thomson experiments on carbon-dioxide, so its accuracy cannot be questioned. The branching curves represent the equation herein derived for ammonia at the pressures 73.48, 102.87, 132.26, and 146.96 pounds per square inch, the upper curve representing the lower pressure. It will be seen that the general trend of the curves is similar, becoming more nearly identical with higher pressures. The circles give the values found by Wobsa at the pressure 29.39 pounds per square inch. His determinations at other pressures are so nearly the same that they would unnecessarily complicate the figure if plotted. The disagreement between these points and the curve of Davis is even greater than between the latter and the branch curves. It is evident, therefore, that Wobsa's data are not in accordance with the law of corresponding states, and are not necessarily to be depended upon; for there is no reason to doubt that ammonia vapor does obey that law. It is expected that the later work of Professor Goodnough and Mr. Mosher, now being carried on, will bring a closer agreement between these curves and that of Davis.

No effort, it must be remembered, was made to bring those last curves into agreement, it being thought that the equations which did express the other properties would show an agreement with the law of corresponding states. That the Agreement is as close as is here shown gives reason for the belief that the equations are essentially of the correct form

and need little change to make them perfectly reliable for all computations.

V.

RESUME' OF FORMULAE.

The formulae with all the contents involved are here given. The pressures are all in pounds per square inch, and the temperatures are absolute in Fahrenheit degrees.

a. For specific volume

$$v = 0.6321 \frac{T}{p} - (1 + 0.0003 p) \frac{8.897 \times 10^{12}}{T^5} - 0.075$$

b. For specific heat

$$c_p = 0.425 + 0.000125 T + \frac{C_1}{T^6} p(1 + 0.00015 p)$$

$$\text{Where } \log C_1 = 13.693949$$

c. For heat content

$$i = 0.425 T + 0.0000625 T^2 - \frac{C_2}{T^5} (1 + 0.00015 p) - 0.013572 p + 345.0$$

$$\text{Where } \log C_2 = 12.994979$$

d. For the Joule - Thomson coefficient

$$\mu = \frac{1}{c_p} \left[\frac{C_2}{T^5} (1 + 0.0003 p) + 0.013572 \right]$$

VI.

SUMMARY OF RESULTS AND CONCLUSIONS.

The need for some such equations in their fully perfected form is great, for the addition they will make to the scientific knowledge of the subject, and because of the extensive use to which ammonia is now being put in cold storage and in ice man-

ufacture. For years designers of refrigerating machinery have been compelled to work with tables of the properties of ammonia which were little better than guess work. But everywhere today the demand is being made for more positive knowledge of this as well as all materials with which the engineer works. This investigation is but in line with those that are being made in all branches of engineering. The results are not perfect, yet they are in many ways an advance over past efforts. The problem is not solved, but an approximate solution has been reached, and a method of solution has been outlined. As however, in other investigations, theory and experiment go hand in hand, and theory after theory is modified as experimental results show fallacies and discrepancies, so, in the work on ammonia vapor, it is essential to a perfect knowledge, or to even a good working knowledge, of the subject that experimental work be done. The gaps in the data have been shown in this discussion. It is hoped that they will soon be filled. They must, however, be filled with accurate data, any other is worse than none. How confusing erring determinations are was shown by the discussions on the values of μ for the law of corresponding states yet until more experimental work has been done, use must be made of that which is at hand, and it is sincerely hoped that the work here shown and the work soon to be finished will be of material assistance in the advancement of the knowledge of this subject.





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